

## RESEARCH ARTICLE

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## Key Points:

- Intraplate volcano Nyiragongo is bromine rich although chlorine poor
- BrO/Br in volcanic plumes depends on initial plume composition
- Determination of Nyiragongo chlorine, bromine, sulfur emission strength

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# Gas emission strength and evolution of the molar ratio of BrO/SO<sub>2</sub> in the plume of Nyiragongo in comparison to Etna

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**Abstract** Airborne and ground-based differential optical absorption spectroscopy observations have been carried out at the volcano Nyiragongo (Democratic Republic of Congo) to measure SO<sub>2</sub> and bromine monoxide (BrO) in the plume in March 2004 and June 2007, respectively. Additionally filter pack and multicomponent gas analyzer system (Multi-GAS) measurements were carried out in June 2007. Our measurements provide valuable information on the chemical composition of the volcanic plume emitted from the lava lake of Nyiragongo. The main interest of this study has been to investigate for the first time the bromine emission flux of Nyiragongo (a rift volcano) and the BrO formation in its volcanic plume. Measurement data and results from a numerical model of the evolution of BrO in Nyiragongo volcanic plume are compared with earlier studies of the volcanic plume of Etna (Italy). Even though the bromine flux from Nyiragongo (2.6 t/d) is slightly greater than that from Etna (1.9 t/d), the BrO/SO<sub>2</sub> ratio (maximum  $7 \times 10^{-5}$ ) is smaller than in the plume of Etna (maximum  $2.1 \times 10^{-4}$ ). A one-dimensional photochemical model to investigate halogen chemistry in the volcanic plumes of Etna and Nyiragongo was initialized using data from Multi-GAS and filter pack measurements. Model runs showed that the differences in the composition of volcanic volatiles led to a smaller fraction of total bromine being present as BrO in the Nyiragongo plume and to a smaller BrO/SO<sub>2</sub> ratio.

## 1. Introduction

Volcanoes inject tens of teragrams of gases like H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, HCl, HF, and solid aerosol particles into the atmosphere, which are able to affect the Earth's radiative balance and climate [e.g., Robock, 2000]. Only relatively recently volcanoes have been considered as significant source for a number of reactive atmospheric trace gases such as reactive halogen species [e.g., Bobrowski et al., 2003; Oppenheimer et al., 2006; von Glasow et al., 2009]. Regarding the impacts on climate, gaseous emissions, especially sulfur compounds, are of much higher importance than the short-lived ash clouds often observed during eruptions [e.g., Robock, 2000]. Volcanic bromine and chlorine emissions can influence the chemistry of the atmosphere [Pinto et al., 1989; Bureau et al., 2000; Halmer et al., 2002; von Glasow et al., 2009; Kutterolf et al., 2013]. For instance, the presence of inorganic bromine in the free troposphere (FT) could have a significant impact on the global tropospheric ozone budget [von Glasow et al., 2004; Lary, 2005; Yang et al., 2005; Theys et al., 2007]. Ground-based, balloon-born, and satellite observations have estimated BrO mixing ratios of 0.5–2 parts per trillion (ppt) assuming an uniform vertical distribution in the absence of strong sources such as present at high latitudes [e.g., Richter et al., 2002]. Little is known about the vertical distribution of BrO in the troposphere [von Glasow and Crutzen, 2007, and references therein; Saiz-Lopez and von Glasow, 2012], and only very few measurements have been carried out in the FT [e.g., Pundt et al., 2002; Theys et al., 2007; Dorf et al., 2008]. Dorf et al. [2008] determined tropospheric BrO between 0 ppt and <1 ppt, which agrees with studies of Schofield et al. [2004, 2006], but is different from other findings [e.g., Richter et al., 1998; Fitzenberger et al., 2000; Salawitch et al., 2005; Theys et al., 2007]. Theys et al. [2007] for instance determined BrO mixing ratios of 2–5 ppt in the free troposphere above Reunion Island. The sources of the estimated tropospheric

background bromine are not fully quantified but are usually assumed to consist mainly of short-lived organic species such as  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ , and  $\text{CHClBr}_2$  [e.g., Dorf *et al.*, 2008; Theys *et al.*, 2011; Parrella *et al.*, 2012; Saiz-Lopez and von Glasow, 2012] and bromine released from sea-salt aerosol. Additionally to degraded organic compounds and sea salt, volcanoes are an additional but ill-quantified source of inorganic bromine, and therefore, the chemistry of halogens in volcanic plumes is being investigated with growing interest. The primary emitted volcanic halogens are assumed to be HCl, HF, and HBr. Trace quantities of HI have also been detected [e.g., Aiuppa *et al.*, 2005]. Unfortunately data for volcanic emissions of the heavier halogens, HBr and HI, are still relatively sparse [e.g., Honda, 1970; Aiuppa *et al.*, 2005; Witt *et al.*, 2008; Wittmer *et al.*, 2014]. The relative abundance of halogens in the gas phase cannot be simply explained by their abundance in the magma. The emission of halogens is often influenced by shallow aquifers, hydrothermal system, and/or subterrestrial brines. In fact, several factors including the individual solubilities of individual halogen compounds in melt and water will affect their emission [e.g., Giggensbach and Sheppard, 1989; Symonds *et al.*, 2001; Aiuppa *et al.*, 2009].

The halogen content of alkaline basalt shows lower values in comparison to subalkaline (tholeiitic) magma. Pinto *et al.* [1989] suggests that halogen emissions could be more abundant in gas emission of increasingly alkaline volcanoes, for example, Etna, El Chichon, and Erebus. Alkaline magma is richer in chlorine and also in sulfur [Woods *et al.*, 1985]. Because of large differences between volcanoes, a global estimate of emissions and the subsequent influence on climate is still difficult to make. Volcanic plume studies are also important to understand the direct impact of volcanic gas emissions on local environments and health impacts [e.g., Delmelle, 2003]. In addition to the investigation of gas emissions and the plume composition of Nyiragongo, which has a magma with exceptional low silica content, this study aims to shed more light on the reactive bromine chemistry in volcanic plumes. Our newly acquired results and related bromine chemistry models are compared with that recently obtained for Etna [Bobrowski *et al.*, 2007], an alkaline volcano known for its (unusually well characterized) large trace halogen emissions [Aiuppa *et al.*, 2005]. We show that, although the two volcanic targets are characterized by rather similar bromine and sulfur emissions, substantial differences in the atmospheric processing of the emitted bromine are unexpectedly observed.

## 2. Nyiragongo

The volcano Nyiragongo belongs to the Virunga volcanic chain. The volcanism at Nyiragongo is caused by the rifting of the Earth's crust where two parts of the African plates are breaking apart. The Virunga volcanic complex consists of eight major volcanoes, from which two are currently considered active: Nyamuragira and Nyiragongo. The volcanism at Virunga started about 11 Ma ago [Ebinger and Furman, 2003]. Nyiragongo is a 3470 m high stratovolcano, with a large summit crater of about 1100 m in diameter, and it is considered with its neighbor Nyamulagira, Democratic Republic of Congo and Erta Ale, Ethiopia, to be among the most active volcanoes in Africa. Satellite measurements showed very large  $\text{SO}_2$  emissions in May 2002, and the observational record indicates that this volcano is one of the largest  $\text{SO}_2$  sources on Earth [Carn, 2004]. Nyiragongo has silica undersaturated mafic lava. The silica contents in its lava flows lies between 38 and 40%. The lava is hypersodic and ultrapotassic [e.g., Rogers *et al.*, 1992, 1998; Chakrabarti *et al.*, 2009].

Even though Nyiragongo is presently one of the most active volcanoes in Africa, it seems that not many eruptions have taken place during the last 1000 years. The only reported and at least partly studied eruptions are those that occurred in 1977 and 2002. Both eruptions were characterized by a short duration (hours to days) and very fast lava flows with an average velocity of about 50 km/h [Durieux, 2003; Komorowski *et al.*, 2004]. At least since 1928 an active lava lake has been situated inside the summit crater [Tazieff, 1975]. During the period of our measurements (2004–2007), the lava lake showed an extent of about  $250 \times 200$  m with a level of around 700 m below the crater rim.

## 3. Measurements, Data Evaluation, and Model Description

On 15 March 2004 and between 18 and 24 June 2007 measurements to determine the composition of the plume of Nyiragongo have been carried out and are described in the following. An overview of the various measurements, used techniques, and measurement dates is given in Table 1.

**Table 1.** Summary of Measurements Presented in This Article and Taken in 2004 and 2007 by Various Measurement Techniques

Date	Measurement Technique	Determined Gas Species	Location
15 March 2004	Mobile DOAS <sup>a</sup>	Ratios: BrO/SO <sub>2</sub> in three distances from the source	Downwind
18–20 and 24 June 2007	Miniaturized scanning DOAS	Ratios: BrO/SO <sub>2</sub> up to two distances	Crater rim
18–24 June 2007	Multi-GAS	Ratios CO <sub>2</sub> /SO <sub>2</sub> and H <sub>2</sub> O/CO <sub>2</sub>	Crater rim
18–24 June 2007	Filter pack samples	Concentration of SO <sub>4</sub> <sup>−</sup> , Br <sup>−</sup> , Cl <sup>−</sup>	Crater rim
March and July 2007	Automated scanning DOAS	SO <sub>2</sub> fluxes	Downwind

<sup>a</sup>DOAS, differential optical absorption spectroscopy.

### 3.1. MAX-DOAS Measurements

From 18 to 24 June 2007, a Mini-multiaxis differential optical absorption spectroscopy (MAX-DOAS) instrument, described in more detail in, e.g., Hönniger *et al.* [2004], Bobrowski *et al.* [2007], or Bobrowski and Platt [2007], was set up on the southern crater rim of Nyiragongo (see Figure 1a).

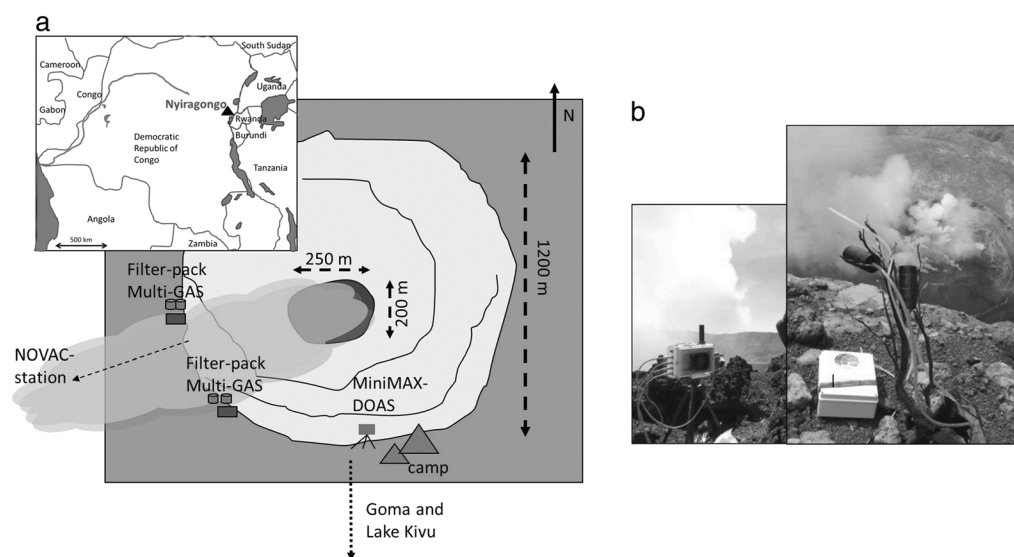
The miniaturized scanning DOAS system (MAX-DOAS) consists of an airtight aluminum box enclosing a commercial miniature UV spectrometer (OceanOptics Inc., USB2000), thermally stabilized with a Peltier element, an entrance optics (quartz lens,  $f = 40$  mm,  $d = 20$  mm, field of view of approximately 0.6°) coupled to a quartz fiber bundle, and an electronic board for the temperature regulation and stepper motor control. The stepper motor is mounted on one side of the metal box, it can be set up on a tripod (Figure 1b), and it moves the metal box to point the entrance optics at different elevation angles over a range of 150°. The instrument can be controlled by a laptop computer. The automatic data acquisition is achieved by using the software package DOASIS [Kraus, 2001].

The wavelength to pixel mapping in a first evaluation run as well as the instrumental line shape were determined by taking a spectrum of a low-pressure mercury emission lamp and using the known mercury spectrum line position to calculate a second-order polynomial for the wavelength to pixel mapping. The wavelength to pixel mapping was later adjusted using the Fraunhofer structure of the measured spectra and comparing it to a high-resolution reference solar spectrum [Kurucz *et al.*, 1984].

In 2007 due to the weather conditions and power limitations, measurements were only carried out for a few hours each on 18–20 and 24 June 2007 and hardly any preliminary data evaluation was carried out at the crater rim. Therefore, several measurement geometries were applied to investigate the plume close to the source in as much detail as possible. On 18 June 2007 the instrument was pointed across the crater into the plume, to measure only at angles close to the horizon (0°, 2°, and 4° elevation) as well as pointed in the opposite direction to take reference spectra (see Figure 2a). On 19 June 2007 the wind was blowing the plume southward enabling the instrument to scan perpendicularly to the plume (see Figure 2b) in 10° steps from a westerly direction at 0° up to 130°. Only for the last measurements on this day, the Mini-MAX-DOAS instrument was scanning alongside the plume (Figure 2c). On 20 and 24 June the plume was scanned perpendicularly again (see Figure 2b), and in the second part of the measurements on 24 June the instrument was pointed across the crater measuring only angles close to the horizon as on 18 June 2007 (see Figure 2a).

For the DOAS fit the software WinDoas v.2.10 from IASB (Belgium Institute for Space Aeronomy [Fayt and Van Roozendaal, 2001]) was used to derive the slant column densities (SCD) of BrO, SO<sub>2</sub>, and NO<sub>2</sub> from the recorded spectra. Since scattered sunlight was used as light source, the solar Fraunhofer lines had to be removed carefully to allow sensitive measurements of trace species. As Fraunhofer reference spectrum (FRS) a background spectrum was used that was taken only shortly after the spectra inside the plume were measured and care was taken that the FRS contained as little as possible absorption by the volcanic plume.

BrO was evaluated in the same manner as in Bobrowski [2005] and Bobrowski and Platt [2007]; therefore, only a brief description is given here. The presented BrO results were obtained from evaluation in the wavelength region from 332 to 352 nm including four BrO absorption bands. A polynomial of second order was chosen to remove the broadband structures. Reference absorption cross-section spectra of BrO, NO<sub>2</sub>, O<sub>3</sub>, SO<sub>2</sub>, O<sub>4</sub>, a “Ring-spectrum” [Bussemer, 1996], and the FRS were simultaneously fitted to the measurement spectra using a nonlinear least squares method [Platt and Stutz, 2008], which is implemented in the evaluation software WinDoas. An example of the evaluation is shown in Figure 3a. SO<sub>2</sub> was analyzed between 362 and 390 nm as described in Bobrowski *et al.* [2010]. Besides SO<sub>2</sub>, two O<sub>3</sub> references absorption cross sections measured at



**Figure 1.** (a) Map of the measurement locations in 2007. The MAX-DOAS location is indicated by a dark square, and the Multi-GAS and filter pack measurement locations are indicated by light grey squares. (b) Photograph of the equipment used in this campaign on the left—MAX-DOAS instrument on the right Multi-GAS and filter pack setup.

223 and 246 K, an  $O_4$  reference and a  $NO_2$  reference at 246 K were also fitted. Also, a Ring spectrum and a Fraunhofer reference spectrum (the closest in time spectrum, measured outside the plume) were fitted. A third-order polynomial was applied to remove the broadband structure and shift, and first-order squeeze were allowed for the measured spectra. An example of the evaluation is shown in Figure 3b.

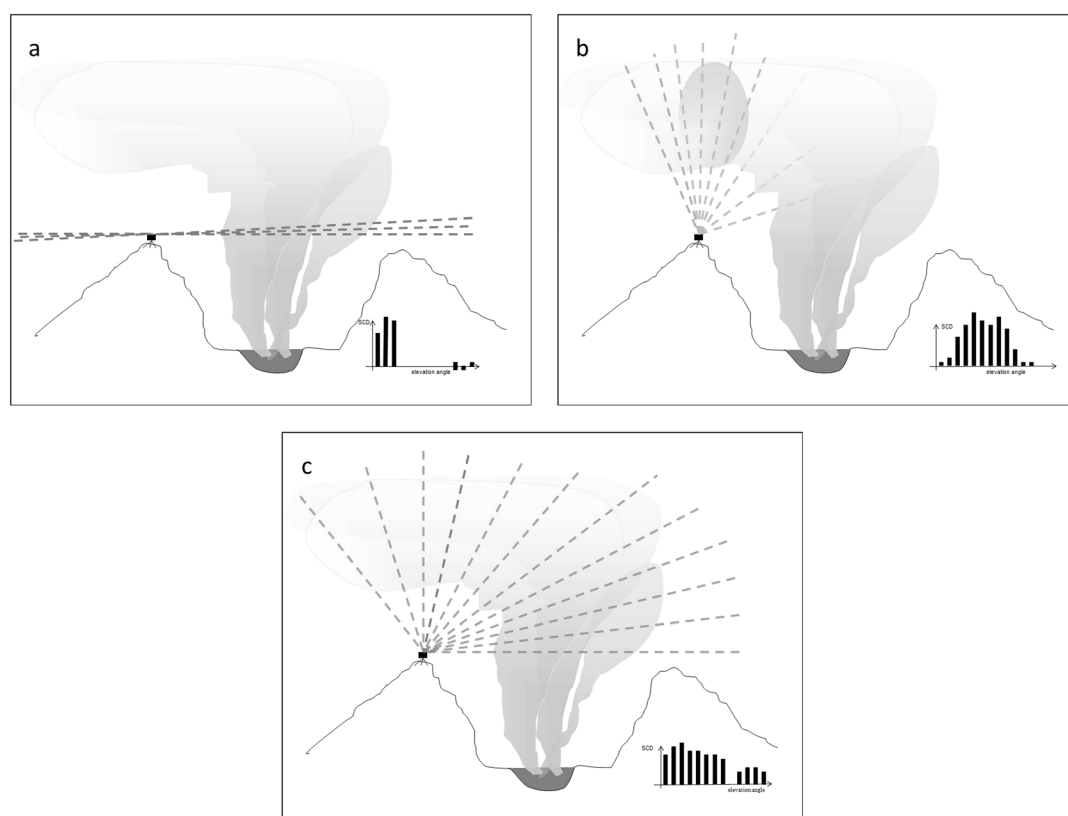
$NO_2$  was analyzed between 402 and 440 nm, where the strongest measured absorption bands of  $NO_2$  for the used spectral range can be found. Hardly any other gas species shows significant structures in this wavelength region, except for IO; therefore,  $NO_2$ , IO, two  $O_3$  references at 223 and 246 K, and a Ring spectrum and a Fraunhofer reference spectrum (the closest in time spectrum, measured outside the plume) were fitted. A fifth-order polynomial was applied to remove the broadband structure and shift, and first-order squeeze were allowed for the measured spectra.  $NO_2$  was also retrieved in the shorter-wavelength regions 399–415 nm and 416–438 nm which lead to similar results. Figure 3c shows only the most promising attempt in the upper wavelength range.

### 3.2. Multi-GAS and Filter Pack Measurements

The mixing ratios of the most abundant volcanic species in the plume of Nyiragongo were determined by simultaneously operating a multicomponent gas analyzer system (Multi-GAS) and the filter pack technique. The Multi-GAS [Shinohara, 2005; Aiuppa *et al.*, 2006] used a LICOR, Inc. NDIR spectrometer (model 840) and a membrapor S-100 electrochemical sensor specific to  $SO_2$ , and allowed the real-time detection of  $H_2O$ ,  $CO_2$ , and  $SO_2$  concentrations in the plume with a 2 s acquisition frequency. The acquired data were then postprocessed (as described in Aiuppa *et al.* [2006]) to calculate gas/gas (e.g.,  $CO_2/SO_2$  and  $H_2O/CO_2$ ) ratios in the plume with a typical uncertainty of  $\leq 10\%$ . The filter packs consisted of three in series base-treated filters contained in a polycarbonate holder, through which plume air was pumped at a constant flow rate of about 5 L/min. The concentrations of the acidic gases ( $SO_2$ , HCl, and HBr) were later determined from the amounts of S, Cl, and Br adsorbed on the filters, as measured by ion chromatography and ICP-MS (see Aiuppa *et al.* [2005] for details). Both Multi-GAS and filter pack determinations were performed daily for seven consecutive days between 18 and 24 June 2007. Table 2 reports the mean concentrations (recalculated on air-free basis) of the above species in the plume over the 7 days of measurements; the compositional variations observed throughout the observational period, and their dependence on the volcano dynamics, are discussed elsewhere [Bobrowski *et al.*, 2013].

### 3.3. NOVAC and Helicopter Instruments

An automated scanning DOAS system has been deployed at the Rusayo station on the southwest flank of Nyiragongo about 10 km from the summit since March 2004, as part of the NOVAC (Network for Observation

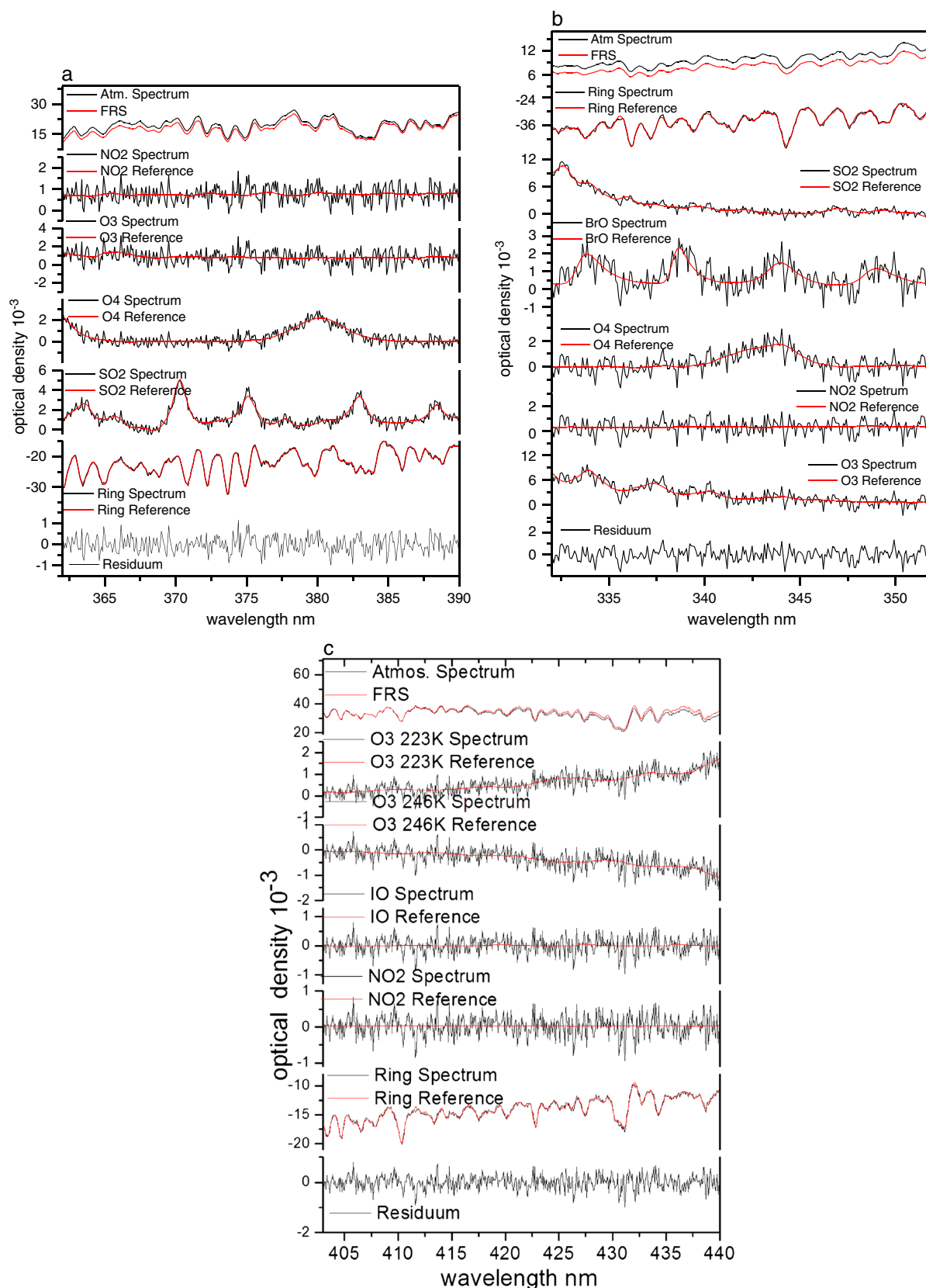


**Figure 2.** Sketch of measurement geometries. (a) Measurements taken straight above the crater rim with low telescope elevation angles ( $0^\circ$ ,  $2^\circ$ , and  $4^\circ$ ) followed by reference measurements taken in the opposite direction at the same elevation angles. In the lower right corner of the sketch the measured slant column densities (SCD) of the trace gases as function of the telescope viewing direction is indicated. (b) The plume is scanned nearly perpendicular starting from one side of the plume to the other side. In the lower right corner of the sketch an example of SCDs of a volcanic trace gas detected in the plume is shown, first nearly nothing observed on one side of the plume, then a rising SCD near to the center of the plume, and finally a decreasing SCD when moving the telescope on the other side of the plume. (c) The plume was at least partly above the instrument; therefore, it could be scanned in the vertical direction, alongside the plume, to gain information of a changing plume composition looking at various distances from the source. First measurements were taken straight above the crater, corresponding to a distance of more or less 500 m from the source, and then enhancing the source distance by increasing the elevation angle. The gas concentrations because of plume dispersion decrease, but trace gas concentration remain still detectable. Similarly, the lower right corner of the sketch illustrates the various SCDs observed for a scan along the plume.

of Volcanic and Atmospheric Change) project [Galle *et al.*, 2010]. This was found to be the best location for the stationary system since the volcanic plume typically disperses west-southwest of Nyiragongo, and hence, under “normal” conditions near-perpendicular scans of the plume can be made. The existing shelter at Rusayo, which houses a seismometer and is under constant surveillance, also provides a secure location for the DOAS system and protects the spectrometer and electronics from the intense tropical solar irradiation. In the scanning DOAS instrument the telescope is attached to a scanning device consisting of a mirror attached to a computer-controlled stepper motor over a range of  $180^\circ$ . Here the scanner was mounted at the end of a hollow iron bar and fixed to the exterior of the hut at Rusayo. The optical fiber and cables connecting the scanning device were fed through the iron bar to the spectrometer inside the hut. The system is powered by solar panels, and data are transferred in real time to the Goma Volcanic Observatory, using a 57,400 baud radio modem. Typically a 1 s integration time was used, with  $3.6^\circ$  angular resolution, providing a full emission measurement every 5 min.

On 15 March 2004, during the period of installation of the NOVAC instrument at Rusayo traverses with a mini-DOAS were carried out from a helicopter, which flew underneath the plume at distances of 5.6 km, 10.2 km, and 16.4 km downwind the crater. The instrument used consisted of a commercial miniature UV





**Figure 3.** Example of a DOAS evaluation for (a)  $\text{SO}_2$ , (b)  $\text{BrO}$ , and (c)  $\text{NO}_2$ . Solid lines: measured spectra, red dotted lines: reference spectra, the atmospheric spectrum was taken at the cloud center ( $\alpha = 30^\circ$ ) on 19 June 2007.

**Table 2.** Plume Composition of Nyiragongo Gained From In Situ Measurements (Multi-GAS and Filter Packs) and Calculated for an Air-Free Environment

H <sub>2</sub> O (%)	CO <sub>2</sub> (%)	SO <sub>2</sub> (%)	Cl (%)	Br (ppm)
48	43	7	0.5	210

spectrometer (OceanOptics Inc., USB2000), a quartz fiber, and a telescope. The instrument was controlled by the software DOASIS [Kraus, 2001] running on a laptop computer. Details of the settings are

described in Galle *et al.* [2003, 2005]. Because of low instrument performance, the BrO/SO<sub>2</sub> ratio was determined only of the center plume spectra of every traverse, where the BrO column optical depth was above the detection limit. BrO and SO<sub>2</sub> SCDs were evaluated as described above in section 3.1.

### 3.4. Atmospheric Chemistry Model

We used a 1-D numerical model to simulate the chemical evolution of the volcanic plume in the atmosphere. The model is the same as used in von Glasow [2010] with minor modifications. Key for the model initialization is the composition of the plume. Based on previous work [Gerlach, 2004; Martin *et al.*, 2006; von Glasow, 2010], we used the thermodynamic equilibrium model HSC to calculate the composition of the mixture of volcanic volatiles and ambient air in the “effective source region” which is located in the crater where temperatures are high enough so that the assumption of immediate thermodynamic equilibrium is still valid but also enough ambient air has been entrained to oxidize the main volcanic reduced gases (mainly H<sub>2</sub>S and H<sub>2</sub>) which leads to a dramatic change in halogen speciation: A large fraction of bromine is then present in photolysable form, kick-starting the bromine explosion. An HCl/SO<sub>2</sub> ratio of 0.07 was chosen for the initialization of the Nyiragongo model run where in comparison to that at Etna an HCl/SO<sub>2</sub> ratio of 0.5 has been used based on an average measured one of about 0.45 [Aiuppa *et al.*, 2002]. For Nyiragongo we used a ratio of volcanic volatiles: ambient air of 91:9 and for Etna 95:5. We chose a ratio that is as rich in volcanic volatiles as possible but where the main buffers have already been oxidized leading to a drastic change in bromine speciation (see discussion in, e.g., Gerlach [2004]); due to the different magmatic composition, this ratio is different for the two volcanoes (see Table 3). Based on the discussion in Martin *et al.* [2012], we set the NO<sub>x</sub> concentrations to zero. The “initial dilution” ratio (see discussion in von Glasow [2010]) was set to 10 for both volcanoes to reproduce measured SO<sub>2</sub> mixing ratios at the crater rim.

As only descriptive meteorological data are available for the duration of the campaigns at Nyiragongo and to be able to focus on differences in the chemical composition of the plume, we used the same meteorological conditions for both cases. The only difference between the model runs is the initial chemical composition of the volcanic plume.

## 4. Results and Discussion

### 4.1. General Plume Composition

Water and carbon dioxide are the two most abundant volcanic volatiles in the Nyiragongo plume. CO<sub>2</sub> mixing ratios in the plume peaked at 720 ppmv and exhibited strong positive correlations with SO<sub>2</sub>, indicating that a clear volcanic signal (peaking at 340 ppmv) was resolved above the background air mixing ratio of 380 ppmv. The volcanic signal was more difficult to distinguish for H<sub>2</sub>O, instead, given its high mixing ratios (11,000–13,000 ppmv) in the local tropospheric air. Our maximum background air-corrected mixing ratios (e.g., in excess to ambient air) resulted of 450 ppmv only. On an air-free basis, the volcanic gas phase is dominated by water and carbon dioxide in almost equal proportions (Table 2), in agreement with previous measurements in magmatic fumarole gases [Gerlach, 1980, 1982] as well as plume measurements [Sawyer *et al.*, 2008]. SO<sub>2</sub> is assumed to be the main sulfur bearing species in the plume; the mixing ratios measured with our Multi-GAS instrument were from below the instrumental detection limit (<0.1 ppmv) to 55 ppmv. On a molar basis, SO<sub>2</sub> accounts for about 7% of the volcanic gas phase (Table 2). Among the open-vent persistently degassing volcanoes, e.g., Erebus [Boichu *et al.*, 2011], Masaya [Horrocks *et al.*, 1999; Witt *et al.*, 2008], Nyiragongo is characterized by low HCl/CO<sub>2</sub> and HCl/SO<sub>2</sub> ratios, which averaged ~0.013 and 0.07, respectively. In contrast, our data support the volcano to be a strong source of bromine: its volcanic gas plume is characterized by HBr/SO<sub>2</sub> and HBr/HCl ratios (averages, ~0.003 and 0.034) that are on the higher end or even above those from Etna ( $7.5 \times 10^{-4}$  to  $3.2 \times 10^{-4}$  and  $\sim 10^{-3}$ , respectively; Aiuppa *et al.* [2005]), volcanic arcs (HBr/HCl between  $1.1 \times 10^{-4}$  and  $7.2 \times 10^{-3}$ ; Gerlach

**Table 3.** Composition of the Effective Source Region Calculated Using HSC for Etna and Nyiragongo<sup>a</sup>

	Etna	Nyiragongo
T (K)	1.31E + 03	1.16e + 03
H <sub>2</sub> O	8.17E − 01	4.54E − 01
SO <sub>2</sub>	2.82E − 02	7.40E − 02
H <sub>2</sub> SO <sub>4</sub>	2.96E − 07	1.04E − 06
SO <sub>3</sub>	2.99E − 05	6.95E − 05
SO	3.10E − 09	8.73E − 10
CO <sub>2</sub>	9.09E − 02	3.92E − 01
CO	1.82E − 07	1.06E − 07
O <sub>3</sub>	4.24e − 13	2.07e − 15
CH <sub>4</sub>	1.05e − 29	1.88e − 31
HCOOH	9.17e − 14	3.75e − 14
H <sub>2</sub> O <sub>2</sub>	4.34e − 09	2.07e − 10
OH	1.46e − 05	9.14E − 07
HO <sub>2</sub>	2.65E − 08	7.73E − 10
NH <sub>3</sub>	2.08E − 14	1.92E − 15
HCl	1.36E − 02	5.17E − 03
HOCl	3.21E − 07	2.98E − 08
Cl <sub>2</sub>	1.29E − 06	1.95E − 07
Cl	1.51E − 05	1.40E − 06
ClO	4.05E − 08	1.42E − 09
HBr	5.08E − 05	1.90E − 04
HOBr	1.20E − 09	1.10E − 09
Br <sub>2</sub>	2.85E − 08	1.06E − 06
BrCl	4.08E − 07	9.78E − 07
Br	1.57E − 05	3.09E − 05
BrO	2.02E − 09	9.85E − 10
Hg	7.50E − 08	0.00E + 00
HgO	3.59E − 10	0.00E + 00
HgCl	6.42E − 13	0.00E + 00
HgCl <sub>2</sub>	1.05E − 10	0.00E + 00
HgBr	3.87E − 14	0.00E + 00
HgBr <sub>2</sub>	2.12E − 13	0.00E + 00

<sup>a</sup>Temperature is given in Kelvin, the composition in mole fraction. No mercury data for the composition of the pure volcanic volatiles were available for Nyiragongo.

[2004, and references therein], Witt *et al.* [2008], Sawyer *et al.* [2011], and Kelly *et al.* [2013]), and in particular other rift and hot spot volcanoes (HBr/HCl between  $5 \times 10^{-4}$  and  $9 \times 10^{-4}$ ; Gerlach [2004]).

## 4.2. SO<sub>2</sub> and BrO

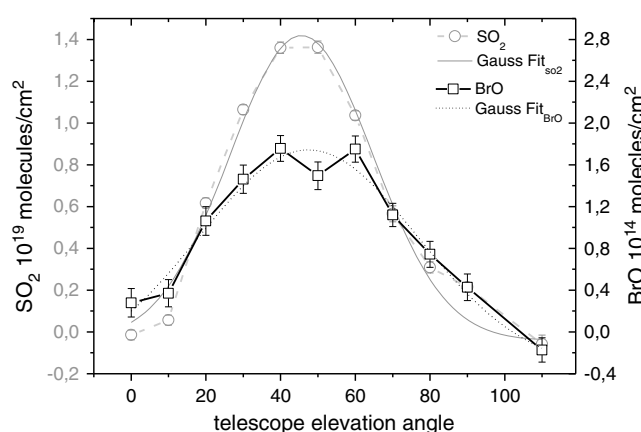
BrO and SO<sub>2</sub> were measured in the young plume of the Nyiragongo lava lake at the summit crater with the MAX-DOAS instrument. Figure 4 shows an example of the slant column densities (SCD) of BrO (blue squares) and SO<sub>2</sub> (red circles) for the different telescope elevation angles of one scan perpendicular to the emitted gas plume carried out close to the volcanic rim on 19 June 2007 (see measurement geometry in Figure 2b). The same type of measurements was undertaken also on 20 and 24 June 2007. On 20 June the measurements took place some meters below the location of the other days on the southern flank of Nyiragongo. Unfortunately on 20 June, the weather changed relatively quickly, and only one plume scan was finalized.

Figure 5 shows as example for correlation graphs, choosing the one with most data points, which were taken on 19 June. The SCDs reach up to  $2.0 \times 10^{14}$  and  $1.8 \times 10^{19}$  molecules/cm<sup>2</sup> for BrO and SO<sub>2</sub>, respectively. NO<sub>2</sub> SCDs

were below  $4 \times 10^{14}$  molecules/cm<sup>2</sup>. Assuming a plume diameter similar to the lake diameter of 250 m would lead therefore to a mixing ratio below 1 ppb for NO<sub>2</sub>. The BrO/SO<sub>2</sub> ratios were calculated for the measurement geometry as shown in Figure 2b, except for 18 June, when only measurements straight above the crater rim had been carried out (Figure 2a). The BrO/SO<sub>2</sub> results are summarized in Table 4. The BrO/SO<sub>2</sub> ratios taken with the same measurement geometry for three different measurement days (19, 20, and 24 June 2007) vary between  $4.6 \times 10^{-6}$  and  $12.5 \times 10^{-6}$ . On 18 June 2007 the BrO/SO<sub>2</sub> ratio was  $2.3 \times 10^{-6}$ . On this day the plume was investigated at a closer point to the emission source due to the different viewing geometry than that of the following days. For this reason the BrO/SO<sub>2</sub> ratio is as expected significantly smaller than on the following measurement days. This can be explained by the BrO formation process in the plume due to the interaction of the volcanic gas with the ambient air [see, e.g., Oppenheimer *et al.*, 2006; Bobrowski *et al.*, 2007; Roberts *et al.*, 2009; von Glasow, 2010]. BrO is not, or perhaps only to a very small amount directly emitted from a volcanic vent. Oppenheimer *et al.* [2006] and Bobrowski *et al.* [2007] already showed that BrO is formed by heterogeneous photochemistry downwind the crater. Bobrowski *et al.* [2007] compared measurement data taken at various distances from the summit of Etna with model studies which resulted in a qualitatively and semiquantitatively good agreement. The increase in BrO in the model is caused by the entrainment of O<sub>3</sub>-rich air into the previously O<sub>3</sub>-free plume and the subsequent start of the “bromine explosion” mechanism [e.g., Platt and Lehner, 1997; Wennberg, 1999].

Also, the variation detected on different days for the same measurement geometry might be explained by plume chemistry taking place within the plume at the same distance from the source but at a different plume





**Figure 4.** Example of results of one plume scan carried out perpendicular to the plume (geometry shown in Figure 2b). The black line and black squares show the BrO SCDs, and the gray dashed line and gray circles show the SO<sub>2</sub> SCDs. Measurements were taken on 19 June 2007.

1998; Aiuppa and Frederico, 2004; Bobrowski and Giuffrida, 2012]. These variations can be explained by the differences in solubility in the melt of the various compounds, and therefore in case of a changing magma level, a changing pressure produces a change in the relative concentration of the exsolved gases.

On 19 June 2007 one scan along the plume was carried out (measurement geometry depicted on Figure 2c). Figure 6 shows the BrO/SO<sub>2</sub> ratios as a function of the different telescope elevation angles, scanning along the plume. An increase of the telescope elevation angles corresponds to a measurement of the plume with an increased age. Similarly to what would be expected from earlier studies [Oppenheimer *et al.*, 2006; Bobrowski *et al.*, 2007], the BrO/SO<sub>2</sub> ratio increases when the plume has spent more time in contact with the surrounding atmosphere.

The BrO/SO<sub>2</sub> ratios measured in 2004 are several times greater than those determined in 2007 (see Table 4). Importantly, all measurements in 2004 were taken at greater distances from the crater rim than the measurements in 2007. Observed BrO/SO<sub>2</sub> ratios increase with distance from the emission source, confirming that the findings from Etna [e.g., Oppenheimer *et al.*, 2006; Bobrowski *et al.*, 2007] are not limited to that volcano. We cannot completely rule out that the higher BrO/SO<sub>2</sub> ratios in 2004 are caused by a difference in the degassing behavior of Nyiragongo. However, the SO<sub>2</sub> emission flux changed only slightly between 2004 and 2007 (S. Arellano *et al.*, manuscript in preparation, 2014), and CO<sub>2</sub>/SO<sub>2</sub> and HCl/SO<sub>2</sub> ratios presented in Sawyer *et al.* [2008] show only short-term (seconds to minutes) temporal fluctuations in the SO<sub>2</sub>–HCl–HF composition, but no general variation between the single investigated years 2005–2007. Our presented measurements average over a time of an hour and will therefore not be sensitive to these changes observed with high temporal resolution. We therefore assume that the main reason for the here observed increase is reactive plume chemistry.

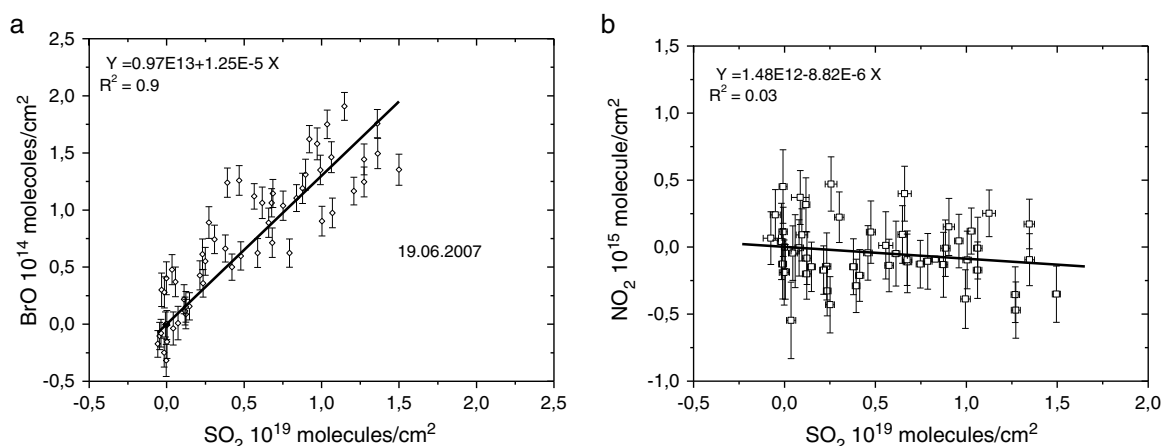
Finally, Figures 7a and 7b show a comparison between Etna data (2004 and 2005) from Bobrowski *et al.* [2007] and Nyiragongo data from 2004 and 2007 as a function of distance (Figure 7a) and time (Figure 7b). The data of Etna for 2004 and 2005 were reevaluated considering a larger wavelength range for the SO<sub>2</sub> evaluation to better take into account nonlinearity effects between the measured optical density and the actual column density as well as problems caused by stray light inside the spectrometer; for a detailed description on the problems of SO<sub>2</sub> evaluation at high SCDs, see, e.g., Bobrowski *et al.* [2010] and Kern [2009].

Although the HBr/SO<sub>2</sub> ratio determined in the plume of Nyiragongo in 2007 has been higher than any reported measurement in the plume of Etna, surprisingly even the highest BrO/SO<sub>2</sub> ratios measured at Nyiragongo are significantly lower than those observed at Etna.

### 4.3. Measurement and Model Comparison

As mentioned above, the BrO/SO<sub>2</sub> ratio was investigated at both volcanoes at several distances downwind showing a rapid increase in BrO/SO<sub>2</sub> before reaching 2 km which corresponds to a plume age

age caused by a difference in wind velocity and/or updraft velocity of the emitted gas. As already described above, BrO is increasing in an aging plume, in particular during the first seconds after emission. Unfortunately, there were no instrumental plume velocity measurements to test this hypothesis. While the changes of the plume age is probably relatively small, the BrO/SO<sub>2</sub> ratio changed by a nonnegligible factor of 2.7. Another interpretation of the data could therefore be a possible change in volcanic/magmatic activity [e.g., Noguchi and Kamiya, 1963; Pennisi and Le Cloarec,



**Figure 5.** Correlation plots from the perpendicular plume scanning geometry on 19 June 2007 (a) BrO as a function of SO<sub>2</sub> SCDs and (b) NO<sub>2</sub> as a function of SO<sub>2</sub> SCDs.

of about 16 min or smaller, assuming a wind velocity of 2 m/s or higher. A wind speed of 2 m/s would be on the very low end of wind speeds at a height of more than 3000 m and has so far only rarely been observed by the authors at both volcanoes. However, assuming a more realistic wind speed of 5 m/s which is reasonable for Nyiragongo (authors' observations in follow-up campaigns 2010 and 2011) and taking a medium wind speed of 10 m/s at Etna (<http://weather.uwyo.edu/upperair/sounding.html> for September/October 2004 and May 2005) distances from the crater have been converted to plume ages which have been used in Figure 7b. Due to the small number of measurement sites, only a coarse time resolution for the evolution of BrO/SO<sub>2</sub> in these two volcanic plumes could be derived. Even though the absolute BrO/SO<sub>2</sub> ratios of both volcanoes are quite different, both measured data sets show a qualitatively similar evolution. According to this, the BrO/SO<sub>2</sub> ratio arguably starts to decrease after about 40 min.

We used the model described in section 3.4 to simulate the chemical evolution of the volcanic plumes of Etna and Nyiragongo. The data shown in Table 3 are used as input of the composition of the volcanic plume in the effective source region. The model is capable of reproducing the overall picture (see Figure 7b) especially the very rapid increase in the BrO/SO<sub>2</sub> ratio even though the BrO/SO<sub>2</sub> ratio is somewhat overestimated for Nyiragongo in the beginning. The model output further shows an increase of the BrO/SO<sub>2</sub> ratios with time (although with a decreasing slope with increasing plume age). This behavior is not observed in our measurements. It is conceivable that a decrease in BrO/SO<sub>2</sub> with time is due to decreases in relative humidity, slowing down heterogeneous cycling of bromine on aerosol particles, but without additional measurements of the plume characteristics, it is impossible to fully address this discrepancy between field data and model output. However, the model reproduces that Etna, which is the volcano with the lower HBr/SO<sub>2</sub> ratio, yields the higher BrO/SO<sub>2</sub> ratio. The bromine speciation of the two model runs is shown in Figure 8 and shows large differences. HBr is converted much quicker into more reactive bromine species in the Etna case compared to Nyiragongo.

In the model the reason for the differences between the two runs are related to two main factors: (1) the absolute amount of SO<sub>2</sub> in the column and (2) the initial speciation of bromine in the effective source region. In the model, the Nyiragongo plume is about 2.6 times as strong in terms of SO<sub>2</sub> column as the Etna plume. Although the Nyiragongo plume is characterized by a higher bromine emission, the BrO column is similar in the model in both runs. This alone leads to a lower SO<sub>2</sub>/BrO ratio in the Nyiragongo plume. The total amount of BrO formed in the column in the model is similar for both volcanoes, but as mentioned above, the fraction of total gaseous bromine that is present as BrO is much higher in the model run for Etna. We tested with further model runs that are not shown here what the role of the initial plume composition is in determining the resulting bromine speciation. To that end the initial plume composition in the Nyiragongo case was changed to resemble the Etna case for sulfur, bromine, and chlorine compounds as well as for HO<sub>x</sub> radicals and all other plume constituents, both individually and in various combinations. Obviously changing the amount of SO<sub>2</sub>, which is a passive tracer at these timescales,

**Table 4.** BrO/SO<sub>2</sub> Molar Ratios of Nyiragongo for the Measurement Days in June 2007 (From the Ground) and in 2004 (From Helicopter)

Date and Source Distance	BrO/SO <sub>2</sub> 10 <sup>-6</sup>
15 March 2004 5.6 km <sup>a</sup>	67 ± 7
15 March 2004 10.2 km <sup>a</sup>	70 ± 7
15 March 2004 16.4 km <sup>a</sup>	45 ± 5
18 June 2007 ~ 700 m	2.3 ± 0.6
19 June 2007 ~ 1000 m	12.5 ± 0.6
20 June 2007 ~ 1000 m	6.8 ± 1.5
24 June 2007 ~ 1000 m	4.6 ± 0.6

<sup>a</sup>Galle et al. [2005].

has a strong impact on the BrO/SO<sub>2</sub>. Other than SO<sub>2</sub> only changes in the initial bromine plume composition changed the ratio BrO/SO<sub>2</sub> noticeably in the model. In order to understand the impact of a higher bromine to sulfur ratio in the Nyiragongo case, we performed an additional model run in which the initial Br<sub>tot</sub>/S ratio was the same as for the Etna case without changing the relative bromine speciation. This increased the fraction

of total bromine that was present as BrO in the modified Nyiragongo plume, compensating for the reduced total amount of bromine in the plume. Keeping the amount of total bromine in the Nyiragongo plume but using the speciation as for Etna for the initial plume composition only changed the partitioning between HBr and Br in the modified Nyiragongo plume without affecting the amount of BrO in the plume. Chemistry in the highly concentrated plume is highly nonlinear, and in the model runs presented here BrO formation is ozone-limited, leading to a high Br atom fraction. Due to the greater amount of total bromine in the Nyiragongo plume, the oxidant limitation is more severe in the Nyiragongo case which is why a smaller fraction of bromine is present as BrO, and counterintuitively, a greater amount of bromine in the Nyiragongo plume leads to the same vertical column of BrO as in the Etna plume (see Figure 8). The background ozone mixing ratios in both runs is 58 ppb (at summit height) which is a typical value according to our own measurements at Etna [Surl et al., 2014]. A higher background mixing ratio of ozone would likely have very minor impacts on oxidant limitation due to the physical size of the plume and slow mixing on the time scale of the measurements. This will be different in every eruption, however, so that ozone measurements are of high priority for future campaigns.

Additionally, we tested whether environmental factors have a significant impact on the results. We investigated the importance of different actinic fluxes and therefore different photolysis rates at the different locations and found this to be unimportant. Likewise, higher ambient humidity as expected in a largely condensed plume in the tropics did not change the BrO/SO<sub>2</sub> ratio noticeably for Nyiragongo.

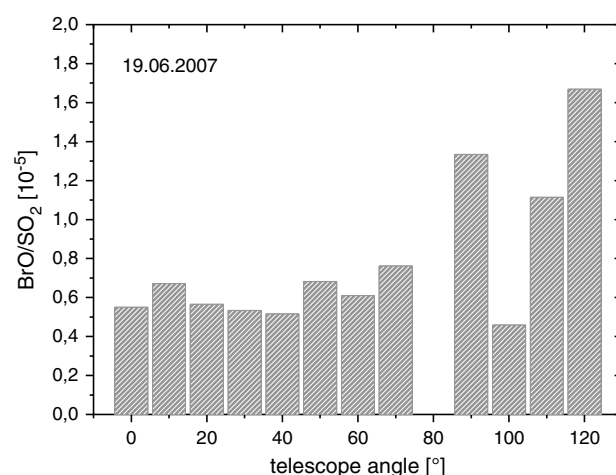
#### 4.4. Estimated Emission Strength

SO<sub>2</sub> flux measurements have been carried out regularly since March 2004 with a stationary scanning DOAS instrument, located at Rusayo [Galle et al., 2005], but unfortunately the system was out of order in April–June

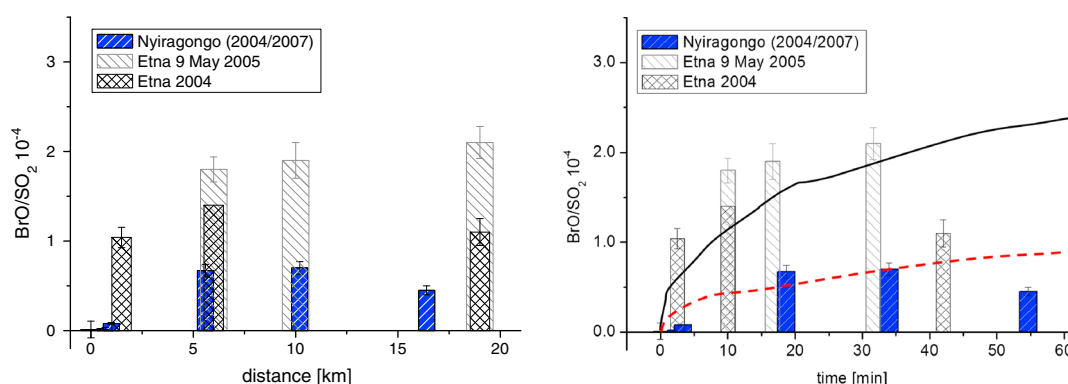
2007. In July 2007 the instrument at Rusayo was repaired and upgraded as part of the NOVAC project ([www.novac-project.eu](http://www.novac-project.eu)). At the same time two additional instruments were installed at Kunene 20 km west and Sake 22 km west-south-west of Nyiragongo.

In March 2007 successful SO<sub>2</sub> flux measurements were carried out on 26 days, giving an average emission of SO<sub>2</sub> of 1900 t/d. In July a 2 day average emission of 800 t/d was determined.

Furthermore, satellite-based observations from the Ozone Mapping Instrument (<http://so2.gsfc.nasa.gov/>) obtained during 18–24 June 2007 provide evidence for a quite stable emission of about 430 t everyday. Since these observations correspond to total emitted mass, its



**Figure 6.** Results of measurements taken alongside the plume. The BrO/SO<sub>2</sub> ratio is clearly increasing with growing source distance, which corresponds to an increasing elevation angle.

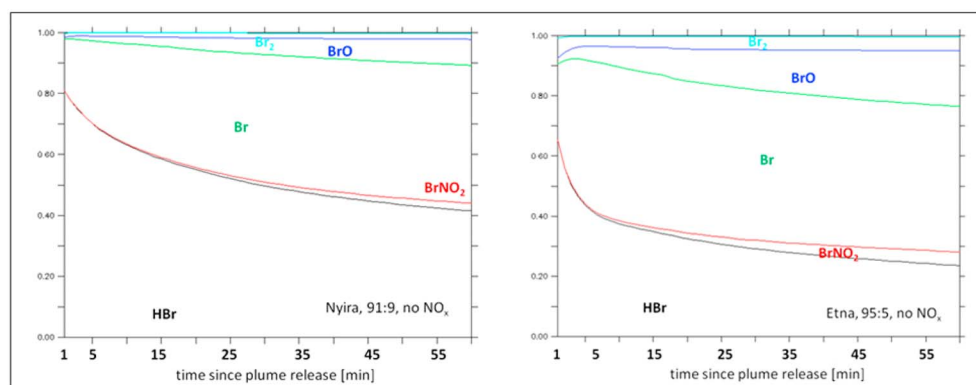


**Figure 7.** (a) BrO/SO<sub>2</sub> ratios for the different measurements at distances up to 19 km from the summit, for Nyiragongo (blue) and Etna (grey). (b) BrO/SO<sub>2</sub> ratios for Nyiragongo (blue) and Etna (grey) shown as a function of estimated plume age for the same measurements presented in Figure 7a (for further information, see the text). Modeled ratio of the vertical column densities of BrO and SO<sub>2</sub>. Etna magmatic setting: black, solid line; Nyiragongo magmatic setting: blue, dashed line. The abscissa shows the time in minutes since plume release.

relation with flux depends on a number of parameters, like plume speed, SO<sub>2</sub> lifetime, spatial resolution, among others, and it is also affected by the plume altitude and presence of clouds. The satellite- and ground-based observations indicate at least the order of magnitude of emission and its stability during a period of quiescent degassing when our measurements took place.

These data can be used to estimate the magnitude of the SO<sub>2</sub> fluxes during the time of our 2007 campaign. Using halogen/sulfur ratios from the filter pack analysis combined with the average SO<sub>2</sub> flux (1300 t/d) of these 2 months yield estimated bromine and chlorine fluxes of 2.6 Br t/d and 52 Cl t/d, respectively.

Apart from the very rough estimation of the SO<sub>2</sub> flux, this is probably only a lower limit estimate of the chlorine and bromine fluxes, not only because the errors of the SO<sub>2</sub> flux measurements is most likely biased toward underestimating the actual values due to the dominance of the “dilution” effect caused by scattering in the foreground [Kern *et al.*, 2010] but also because several species such as HOCl, HOBr, Br<sub>2</sub>, Cl<sub>2</sub>, ClO, BrCl, BrNO<sub>2</sub>, BrNO<sub>3</sub>, and ClNO<sub>2</sub> might not be taken up with 100% efficiency into the filter packs [e.g., Lazrus *et al.*, 1976; Sedlacek *et al.*, 1984; Kitto and Anderson, 1988; Sturges *et al.*, 1993] and could definitively have a nonnegligible contribution. One of the very few measurements in the tropical free troposphere carried out on a balloon by Dorf *et al.* [2008] could not detect any BrO below 15 km. Other authors [e.g., Theys *et al.*, 2007, 2011] who investigated the BrO concentration in the troposphere could detect BrO in the tropical free troposphere with a maximum at around 6 km. Nearby, local sources might be responsible for these findings. Based on our data, volcanic sources of bromine that act in the free troposphere due to the summit height of the volcanoes can be significant sources of bromine. In the tropics volcanic bromine might also be transported into the stratosphere in deep convection events.



**Figure 8.** Relative speciation of bromine in the core of the plume. Shown are the relative contributions of several bromine compounds to the sum of gas phase bromine. (a) Nyiragongo and (b) Etna.

The bromine and chlorine fluxes of Nyiragongo estimated here are significant compared to estimates of the global volcanic arc HCl and HBr emissions of 12 kt/d and 13–41 t/d, respectively [Pyle and Mather, 2009]. In particular, its bromine flux might correspond to up to 20% of this estimated global volcanic emissions, but a proper quantification of course requires more extensive data sets regarding Nyiragongo itself and also the global volcanic bromine emission estimates. Global estimates are currently based on only very few data points for bromine, which usually stem from brief field campaigns and partly consist of single data points for some volcanoes. Also, our Br/S data were taken during a 1 week sampling campaign, and it might be questionable how representative the ratio is over longer time periods. Nevertheless, the data presented here show that Nyiragongo is a notable inorganic halogen and sulfur source for the free troposphere.

## 5. Conclusion and Outlook

First studies of the bromine and sulfur distributions in the plume of Nyiragongo have been presented. These data show that even if chlorine abundances in a volcanic gas plume might be very low in interplate volcanism, this is not necessarily true for other halogens, especially bromine. This further suggests that the origin of the volcanic bromine source is probably not only the Earth's crust, because Nyiragongo is likely fed by magma originating from a depth >150 km [e.g., Chakrabarti et al., 2009].

The fluxes of halogens and sulfur to the free troposphere emitted from the lava lake of Nyiragongo were estimated to about 1300 SO<sub>2</sub> t/d, 2.6 HBr t/d, and 52 HCl t/d. Nyiragongo is therefore a so far unconsidered, but significant source of inorganic bromine to the free troposphere.

Nyiragongo's plume is relatively poor in filterable chlorine but richer in bromine than Etna and even has a higher HBr/SO<sub>2</sub> ratio than the highest globally considered one—Soufriere Hills [Gerlach, 2004]. One of our main findings is that even though Nyiragongo has a greater Br/S ratio in its volcanic plume than Etna, the BrO/SO<sub>2</sub> ratios downwind show smaller values in the aged Nyiragongo plume in comparison to the plume of Etna. Model studies could reproduce this result and suggested that this might be (a) due to the greater amount of SO<sub>2</sub> in the Nyiragongo plume and (b) due to the different bromine speciation in the effective source region leading to changes in the nonlinear plume chemistry resulting in similar vertical columns of BrO in the model runs for both volcanoes.

In order to improve our quantitative understanding of processes in the volcanic plume, the plume should be probed simultaneously over a broader range of plume ages. Furthermore, the composition of the volcanic plume close to the emission source should be quantified in more detail, analyzing as many compounds as possible of particular interest would be the abundance of, e.g., OH, HO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>, and further reactive halogen compounds (such as HOBr, Br<sub>2</sub>, Cl<sub>2</sub>, BrCl, and BrNO<sub>3</sub>). It is also important to note that BrO and SO<sub>2</sub> measurements alone do not provide enough information to test model results, such as the ones presented here, in detail. Attempts should be undertaken to quantify the speciation of bromine in volcanic plumes, which could in principle be done using airborne chemical ionization mass spectrometry. Meteorological data, especially wind speed, and standard atmospheric chemistry data, foremost ozone, should also be measured in the plume.

The reason for the notable difference of the bromine/chlorine abundance of Nyiragongo in comparison to most other studied volcanic composition needs to be investigated.

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